C E R T I F I C A T I O N

I, Takashi KOJIMA of Ginza Ohtsuka Bldg., 2F, 16-12, Ginza 2-chome, Chuo-ku, Tokyo, Japan, hereby certify that I am the translator of the accompanying certified official copy of the documents in respect of an application for a patent filed in Japan on the 8th of March, 2001 and of the official certificate attached thereto, and certify that the following is a true and correct translation to the best of my knowledge and belief.

Dated this 5th day of January, 2004

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(Translation)

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Applicant(s) : Shin-Etsu Chemical Co., Ltd.

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[SPECIFICATION]

[TITLE OF THE INVENTION] Thermal Spray Spherical Particles, and Making Method

[CLAIMS]

[Claim 1] Spherical particles for thermal spraying, characterized in that the particles consist essentially of a rare earth(inclusive of yttrium) oxide or aluminum oxide and have a breaking strength of at least 10 MPa and an average particle diameter of 15 to 100 μm.

[Claim 2] The spherical particles of claim 1 characterized in that said rare earth oxide is yttrium oxide or ytterbium oxide.

[Claim 3] A method for preparing spherical particles for thermal spraying of claim 1, characterized in that rare earth oxide fines having a Fisher diameter of up to 0.6 μm are granulated into granules, and the granules are fired at a temperature of 1,500 to 1,800°C.

[Claim 4] A method for preparing spherical particles for thermal spraying of claim 1, characterized in that aluminum oxide fines having a Fisher diameter of up to 0.6 μm are granulated into granules, and the granules are fired at a temperature of 1,300 to 1,500°C.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field of the Invention]

This invention relates to thermal spray spherical particles of rare earth oxide or aluminum oxide useful for thermal spraying on ceramics etc., and a method for making the same.

[0002]

[Prior Art]

From the past, plasma spraying and detonation spraying techniques have been widely utilized for forming dense spray coatings on surfaces of ceramic.

Yttrium oxide, ytterbium oxide, aluminum oxide etc. are used as a starting material of thermal spraying particle powders used for thermal spraying to impart corrosion resistance to the surface of the coated component.

The particle powders suitable for thermal spray coatings are obtained by the methods such as a method of melting and grinding a material, followed by classification; a method of firing a raw material and pulverizing the sintered material, followed by classification; and a method of granulating a material and firing the particles. Of these, thermal spray particle powders obtained by granulating and firing the particles usually have spherical shape, which is most suitable for thermal spraying. Thus, the thermal spraying particle powders generally prepared by this method are widely used.

[0003]

[Problem to be solved by the Invention]

However, thermal spraying particles obtained by granulating and firing as described above tend to have a lower breaking strength compared to those of the particles obtained by other methods. When such particles are introduced in the flame (or plasma), the particles are easily collapsed into fines. As a result, they may remain unmelted during the spraying step because of insufficient amount of heat acquired. Thus, such unmelted particles or fines collide with the substrate to be spray coated so that the fines are incorporated in or stick to the sprayed coating, failing to form a satisfactory coating.

[0004]

The present invention has been accomplished under the above circumstances. An object of the invention is to provide thermal spray spherical particles which have a sufficient breaking strength to remain uncollapsed in the flame (or plasma) during spraying, and a preparation method thereof.

[0005]

[Means for solving the problem and Embodiment of the Invention]

The inventors have earnestly studied to attain the above objects and have found that spherical particles for thermal spraying, consisting essentially of rare earth (inclusive of yttrium) oxide or aluminum oxide and having a specific breaking strength and an average particle diameter do not collapse in the spraying flame (or plasma) and thus form a coating in which no unmelted fragments are incorporated into or on the surface of coating. Especially, by processing a starting oxide powder under predetermined conditions, thermal spray particles having the desired physical properties are produced.

[0006]

Accordingly, the present invention provides:

(1) Spherical particles for thermal spraying, characterized in that the particles consist essentially of a rare earth(inclusive of yttrium) oxide or aluminum oxide and have a breaking strength of at least 10 MPa and an average particle diameter of 15 to 100 μm.

(2) The spherical particles of (1) characterized in that said rare earth oxide is yttrium oxide or ytterbium oxide.

(3) A method for preparing spherical particles for thermal spraying of (1), characterized in that rare earth oxide fines having a Fisher diameter of up to 0.6 μm are granulated into granules, and the granules are fired at a temperature of 1,500 to 1,800° C.

(4) A method for preparing spherical particles for thermal spraying of (1), characterized in that aluminum oxide fines having a Fisher diameter of up to 0.6 μm are granulated into granules, and the granules are fired at a temperature of 1,300 to 1,500° C.

[0007]

As used herein, the "breaking strength" St is determined from the following equation using as parameters a compression load (N) and a particle diameter (mm) measured by

a micro-compression testing instrument (MCTM-500 by Shimadzu Corp.).

$$St = 2.8P/\pi d^2$$

As used herein, the "average particle diameter" is a diameter D50 as measured by a laser diffraction analyzer. Fisher diameter is as measured by a Fisher subsieve sizer.

[0008]

Following is a detailed description of the invention.

As used herein, the term rare earth oxide of which the thermal spray spherical particles consist encompasses oxide of rare earth of Group 3A in the Periodic Table inclusive of yttrium (Y). Of these oxides, yttrium oxide and ytterbium oxide are more preferred.

It is understood that compound oxides of the rare earth combined with at least one metal selected from Al, Si, Zr, In, etc. are also useful for the inventive particles.

If the breaking strength St of thermal spray spherical particles is less than 10 MPa, the particles will collapse into fines in the flame (or plasma) during the spraying step. The upper limit of breaking strength is, though not critical, usually up to 300 MPa.

If the average particle diameter of thermal spray spherical particles is less than 15 μm, some particles may gasify, resulting in a reduced yield. If the average particle diameter is more than 100 μm, some particles may remain unmelted during the spraying step. The preferred average particle diameter is from 20 to 80 μm.

[0009]

Of the thermal spraying spherical particles, the thermal spraying spherical particles of rare earth oxide are prepared by granulating rare earth oxide fines having a Fisher diameter of up to 0.6 μm into granules, and firing the granules at a temperature of 1,500 to 1,800°C.

The thermal spraying spherical particles of aluminum oxide are prepared by granulating aluminum oxide fines having

a Fisher diameter of up to 0.6 μm into granules, and firing the granules at a temperature of 1,300 to 1,500° C.

[0010]

If the Fisher diameters of rare earth oxide and aluminum oxide fines are more than 0.6 μm, the sintering of granules in the firing step after granulating step is retarded, failing to produce spherical particles with a satisfactory breaking strength. With an improvement in breaking strength taken into account, the preferred Fisher diameter is 0.4 μm or less.

For granulation, any well-known technique may be employed. For example, granulation is carried out using a slurry of fines having a Fisher diameter of up to 0.6 μm in a suitable solvent. The solvent used to form the slurry is not critical and may be selected from alcohols such as isopropanol, water and other solvents.

The resulting granules may have an appropriate size, and preferably an average particle diameter of 15 to 100 μm, especially 20 to 100 μm because particles suited for thermal spraying are obtainable therefrom at the end of firing.

[0011]

According to the inventive method, the firing step is carried out in an atmosphere of air, an inert gas or vacuum, using an electric furnace or the like. The firing temperature is 1,500 to 1,800° C, more preferably 1,500 to 1,700° C when the rare earth oxide is used as the raw material.

The firing temperature is 1,300 to 1,500° C, when the aluminum oxide is used as the raw material.

A firing temperature below the lower limit (1,500 or 1,300° C) might lead failure of obtaining the thermal spraying spherical particles with high enough breaking strength. A firing temperature above the upper limit (1,800 or 1,500° C) might cause substantial fusion of particles, failing to obtain spherical particles.

[0012]

More specifically, the thermal spray spherical particles are prepared by the procedure to be described below.

First, a slurry is prepared by adding a solvent such as water to a fine powder of rare earth oxide or aluminum oxide having a Fisher diameter of up to 0.6 μm. Granules are then formed from the slurry using a granulator such as a tumbling granulator (i.e., rotary disk granulator), spray granulator, compression granulator or fluidized bed granulator. A granular powder having an average particle diameter of 15 to 100 μm is obtained.

[0013]

By way of precaution for preventing the granules from being broken during collection or other operation, an organic material which will be burnt out in the firing step may be blended in the raw material oxide prior to granulation. Examples of the organic material include polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC), polyvinyl pyrrolidone (PVP), methyl cellulose (MC), hydroxypropyl cellulose (HPC), polyethylene glycol, phenolic resins, and epoxy resins. The amount of the organic material added is not critical as long as it gives rise to no problem in the firing step. Usually, the organic material is added in an amount of 0.1 to 3% by weight based on the rare earth oxide fine powder or aluminum oxide fine powder.

In the granulation step by a granulator, more or less non-spherical granules form. Since such non-spherical granules can cause to reduce the flow of powder, it is recommended to separate the granulated powder into non-spherical granules and spherical granules by means of a classifier, and to deliver only the spherical granule fraction to the firing step.

[0014]

The thus granulated powder is placed in a refractory container and loaded in an electric furnace or the like in which it is fired in an atmosphere of air, an inert gas or vacuum at a temperature of 1,500-1,800° C (in case of rare

earth oxide) or at a temperature of 1,300-1,500°C (in case of aluminum oxide) for 5 to 300 minutes.

The firing step yields thermal spraying spherical particles which are ready for use in thermal spraying. In the particles as fired, however, some fusion bonds between particles are usually found. If the particles in this partially fused state are exposed to high-temperature plasma, melting is insufficient on the coarse particle side, resulting in less adhesion to the substrate. It is thus recommended to feed the particles as fired to a disintegrator, pulverizer or classifier such as sieve, whereby fused particles are separated into discrete monodisperse particles that are thermal spray spherical particles with an average particle diameter of 15 to 100 μm.

[0015]

The thermal spray spherical particles obtained by the above procedure have a sufficiently high breaking strength of at least 10 MPa to withstand rupture during the spraying step. Using the particles for thermal spraying, there is obtained a sprayed coating in a sound state that unmelted fines are not incorporated in the coating or do not stick to the coating surface.

[0016]

When thermal spraying the particles to the substrate surface, plasma spraying or vacuum plasma spraying method is used. The material of the substrate is usually selected from aluminum, nickel, chromium, zinc, zirconium, and alloys thereof, alumina, aluminum nitride, silicon nitride, silicon carbide, quartz glass, and zirconia.

[0017]

[EXAMPLE]

Examples of the invention and Comparative Examples are given below by way of illustration and not by way of limitation.

[0018]

[Example 1]

10 g of methyl cellulose was added to 5 kg of yttrium oxide having a Fisher diameter of 0.45 μm, to which deionized water was added to give an approximately 40 wt% aqueous slurry. The aqueous slurry was sprayed by a spray dryer, forming granules having an average particle diameter of about 50 μm.

The granule powder was fired in an electric furnace having an air atmosphere at 1,600°C for 2 hours and cooled. The thus obtained powder was passed through a sieve with an opening of 150 μm, obtaining a thermal spray powder of spherical particles having an average particle diameter of 50 μm. The thermal spraying spherical particles had a breaking strength of about 13 MPa.

The breaking strength is measured using a planar indenter at a testing load of 980 mN and a load applying rate of about 41.5 mN/sec.

[0019]

[Example 2]

Thermal spray spherical particles having an average particle diameter of 50 μm were prepared as in Example 1 except that yttrium oxide having a Fisher diameter of 0.28 μm was used. The thermal spray spherical particles were measured to have a breaking strength of about 160 MPa.

[0020]

[Example 3]

Thermal spray spherical particles having an average particle diameter of 49 μm were prepared as in Example 1 except that yttrium oxide having a Fisher diameter of 0.35 μm was used. The thermal spray spherical particles were measured to have a breaking strength of about 130 MPa.

[0021]

[Example 4]

Thermal spray spherical particles having an average particle diameter of 50 μm were prepared as in Example 1 except that ytterbium oxide having a Fisher diameter of 0.28

μm was used. The thermal spray spherical particles were measured to have a breaking strength of about 160 MPa.

[0022]

[Example 5]

Thermal spray spherical particles having an average particle diameter of 50 μm were prepared as in Example 1 except that ytterbium oxide having a Fisher diameter of 0.30 μm was used. The thermal spray spherical particles were measured to have a breaking strength of about 120 MPa.

[0023]

[Example 6]

Thermal spray spherical particles having an average particle diameter of 50 μm were prepared as in Example 1 except that aluminum oxide having a Fisher diameter of 0.20 μm was fired at a temperature of 1,350°C. The thermal spray spherical particles were measured to have a breaking strength of about 130 MPa.

[0024]

[Example 7]

Thermal spray spherical particles having an average particle diameter of 50 μm were prepared as in Example 1 except that aluminum oxide having a Fisher diameter of 0.30 μm was fired at a temperature of 1,300°C. The thermal spray spherical particles were measured to have a breaking strength of about 150 MPa.

[0025]

[Comparative Example 1]

Thermal spray spherical particles having an average particle diameter of 50 μm were prepared as in Example 1 except that yttrium oxide having a Fisher diameter of 0.8 μm was used. The thermal spray spherical particles were measured to have a breaking strength of about 3 MPa.

[0026]

[Comparative Example 2]

Thermal spray spherical particles having an average particle diameter of 50 μm were prepared as in Example 1 except that yttrium oxide was fired at a temperature of 1,250° C. The thermal spray spherical particles were measured to have a breaking strength of about 2 MPa.

[0027]

[Comparative Example 3]

Thermal spray spherical particles were not obtained though the procedure in Example 1 was repeated except that yttrium oxide was fired at a temperature of 1,850° C.

[0028]

[Comparative Example 4]

Thermal spray spherical particles having an average particle diameter of 50 μm were prepared as in Example 1 except that ytterbium oxide having a Fisher diameter of 0.82 μm was used. The thermal spray spherical particles were measured to have a breaking strength of about 4 MPa.

[0029]

[Comparative Example 5]

Thermal spray spherical particles having an average particle diameter of 50 μm were prepared as in Example 1 except that aluminum oxide having a Fisher diameter of 1.00 μm was fired at a temperature of 1,300° C. The thermal spray spherical particles were measured to have a breaking strength of about 5 MPa.

[0030]

[Comparative Example 6]

Thermal spray spherical particles having an average particle diameter of 50 μm were prepared as in Example 1 except that aluminum oxide having a Fisher diameter of 0.20 μm was fired at a temperature of 1,200° C. The thermal spray spherical particles were measured to have a breaking strength of about 3 MPa.

[0031]

Table 1 summarizes the type and Fisher diameter of the starting powder, the firing temperature, and the average particle diameter and breaking strength of thermal spray spherical particles in the foregoing Examples and Comparative Examples.

[0032]

[Table 1]

	Starting powder	Fisher diameter (μm)	Firing temperature (°C)	Average diameter of thermal spraying particle (μm)	Breaking strength (MPa)
Example 1	yttrium oxide	0.45	1600	50	13
Example 2	yttrium oxide	0.28	1600	50	160
Example 3	yttrium oxide	0.35	1600	49	130
Example 4	ytterbium oxide	0.28	1600	50	160
Example 5	ytterbium oxide	0.30	1600	50	120
Example 6	aluminum oxide	0.20	1350	50	130
Example 7	aluminum oxide	0.30	1300	50	150
Comparative Example 1	yttrium oxide	0.80	1600	50	3
Comparative Example 2	yttrium oxide	0.45	1250	50	2
Comparative Example 3	yttrium oxide	0.45	1850	--	--
Comparative Example 4	ytterbium oxide	0.82	1600	50	4
Comparative Example 5	aluminum oxide	1.00	1300	50	5
Comparative Example 6	aluminum oxide	0.20	1200	50	3

[0033]

As seen from the results of Examples and Comparative Examples, spray spherical particles prepared using a starting oxide powder having a Fisher diameter of more than 0.6 μm had a breaking strength of less than 10 MPa, and spray spherical particles prepared using a starting oxide powder having a

Fisher diameter of 0.6 μm or less had a breaking strength of more than 10 MPa and sometimes (in Examples 2-7) more than 50 MPa.

Using a plasma spraying torch, the spray particles obtained in Examples and Comparative Examples were sprayed to alumina ceramic substrates. When the spray particles having a breaking strength of more than 10 MPa in Examples were used, no fines resulting from rupture of particles developed during the spraying and good sprayed coatings were obtained.

[0034]

[Effect of the Invention]

Since the thermal spray spherical particles are formed of rare earth (inclusive of yttrium) oxide or aluminum oxide and have a breaking strength of at least 10 MPa and an average particle diameter of 15 to 100 μm according to the present invention, they do not collapse into fines in the spraying flame (or plasma) of flame spraying or plasma spraying to form a coating. By spraying the particles, there is obtained a satisfactory coating having no fines stuck to its surface.

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[ABSTRACT]

[Problem]

To provide thermal spray spherical particles which have a sufficient breaking strength to remain uncollapsed in the flame (or plasma) during spraying, and a preparation method thereof.

[Means for Solution]

Spherical particles for thermal spraying, consisting essentially of a rare earth (inclusive of yttrium) oxide or aluminum oxide and have a breaking strength of at least 10 MPa and an average particle diameter of 15 to 100 μm.

[Selected Drawing] None